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(71) Applicants
Daimler-Benz
Aktiengesellschaft,
Stuttgart-Untertürkheim,
Federal Republic of
Germany
(72) Inventors
Jörg Abthoff,
Hans-Dieter Schuster,
Günter Loose,
Michael-Rainer Busch
(74) Agents
Jensen & Son, 8, Fulwood
Place, High Holborn,
London WC1V 6HG

(54) Electrochemical sensor with protective device for determining oxygen content in exhaust

(57) In an electrochemical measuring sensor for determining the oxygen content in exhaust gases, the part of the sensor 1 which is exposed to the exhaust gases is surrounded by a protective device 12 spaced from the sensor, which device consists of a porous tube of sintered metallic or ceramic material. Suitably, the tube is spaced from the sensor by 0.01 to 20.0 mm and has a wall thickness of not less than 1.5 mm, if of ceramic material, and 1 mm, if of metallic material, the pore size being from 5 to 800 microns. The inner surfaces of the pores may be lined with a catalyst material for accelerating the establishment of gas equilibrium.

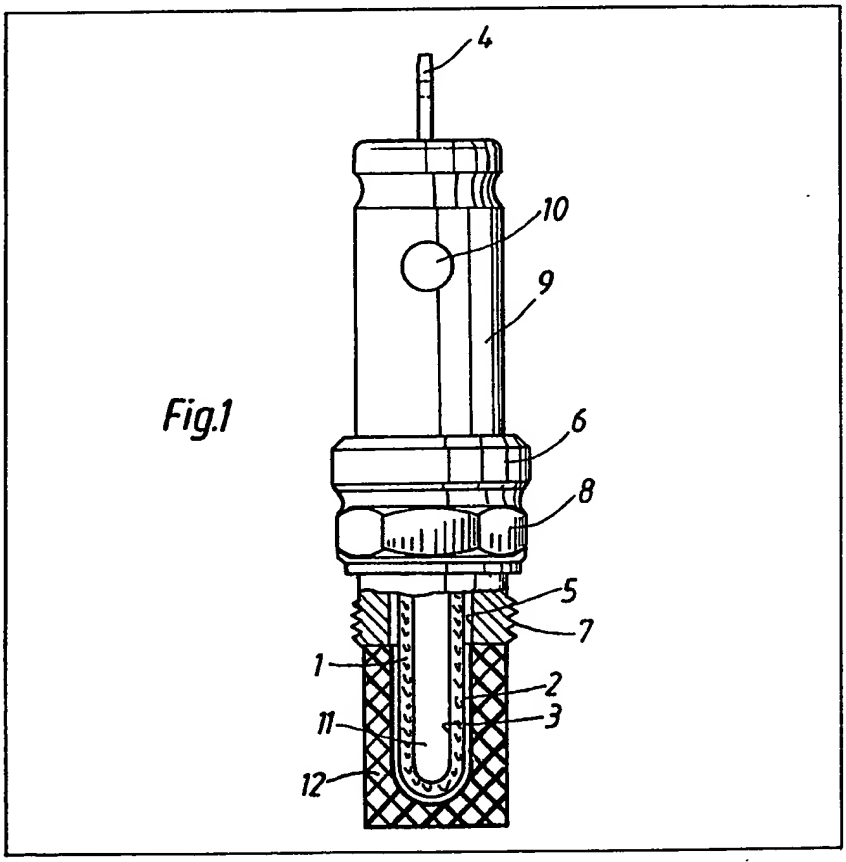

Fig.1

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Fig.1

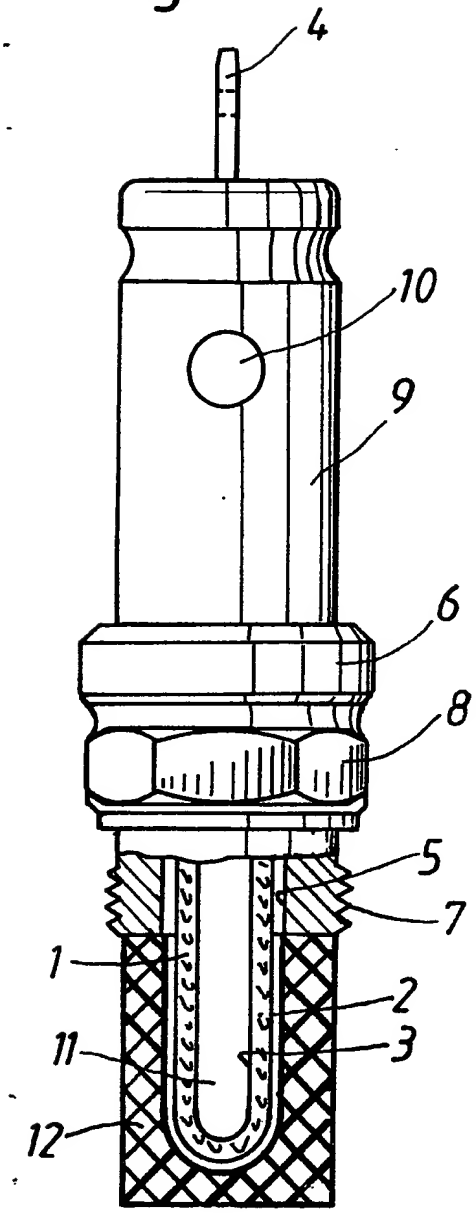


Fig.2

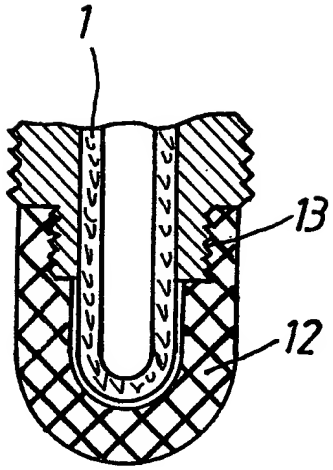
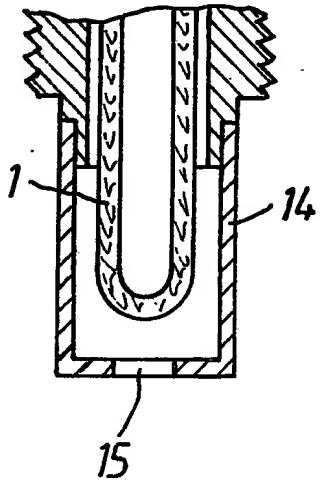


Fig.3



SPECIFICATION

Electrochemical sensor for determining oxygen content in exhaust gases

The invention relates to an electrochemical measuring sensor for determining oxygen content in exhaust or waste gases, (hereinafter referred to as exhaust gases), especially gases from internal-combustion engines, in which part of the sensor exposed to the gases is surrounded by a protective device which has openings and is spaced from the sensor.

Sensors for determining the oxygen concentration in the exhaust gases of an internal-combustion engine for the purpose of controlling the air-fuel ratio of the mixture supplied to the engine are known, for example, from German Offenlegungsschriften 2,433,158, 2,502,409 and 2,639,097, US Patent Specification 3,759,232, German Auslegeschrift 2,657,437 and "Automotive Engineering" 87 (3), pages 88 to 97 (March 1979).

In one form, these sensors have a solid tubular electrolyte which conducts oxygen ions, thin-layer platinum electrodes being formed, by thermal vapour-deposition, cathode sputtering, deposition from the gas phase, chemical reduction, electro-deposition or the like, on the inside exposed to a reference gas and on the outside exposed to the exhaust gases, respectively, of the solid electrolyte. Between the platinum electrodes, an electromotive force corresponding to the difference between the oxygen concentrations or partial pressures of the exhaust gases and of the reference gas is generated and can be measured. In another form, the sensors are made of a ceramic titanium material (TiO_2), sometimes impregnated with precious metal, whose electrical resistance changes with the oxygen content of the gaseous medium and with temperature.

To lengthen the life of such a sensor, the part exposed to the exhaust gases is surrounded by a protective device.

With known electrochemical sensors, the part exposed to the exhaust gases is provided with a protective sleeve which has a number of openings (German Offenlegungsschriften 2,315,444, 2,639,097 and 2,627,760. However, the catalyst layer on the outside of the sensor is quickly destroyed because the stream of exhaust gases enters through the openings and, together with coarse particles carried by it, strikes the catalyst layer directly. Moreover, the sensor region, with its catalyst layer, located behind the openings is not protected against shock effects which occur upon sudden temperature or pressure changes in the inflowing exhaust gases.

Also known are tubular protective devices which are closed at one end and have several openings in their cylindrical shell and deflecting means intended to prevent the incoming gas from striking the solid-electrolyte tube directly. With these protective devices, the temperature gradient at the electrolyte tube is still very high and the useful life of such sensors is endagered (German Offenlegungsschrift 2,452,924 and German Auslegeschrift 2,553,212).

In another protective device, two coaxial tubes provided with holes are disposed, spaced from each other, around the solid electrolyte tube, the holes in the tubes being offset in relation to each other (German Offenlegungsschrift 2,348,505).

Although these protective devices have achieved a certain measure of protection against mechanical attack and also against temperature and pressure shocks, they are unsatisfactory from the standpoint of adequate life of the sensor with its catalyst layer, on the one hand because of the large temperature gradient between the part of the sensor which is preferentially swept by exhaust gas and the part thereof which is swept only indirectly by exhaust gas and, on the other hand and in particular, because the protective devices cannot prevent the catalyst from being rendered inactive by catalyst poisons such as sulphur, phosphorus and, especially, lead or lead compounds when lead-containing petrol is used.

It is therefore advisable, with vehicles having sensors of this type, to use lead-free petrol, but, as lead-free petrol is not obtainable everywhere, the range of operation of such vehicles is restricted.

The present invention seeks to provide a protective device which not only protects the measuring sensor against mechanical attack as well as against temperature and pressure shocks, but also ensures a satisfactory life of the sensor even when used in lead-containing exhaust gases.

According to the invention, in an electrochemical measuring sensor for determining the oxygen content in exhaust gases, the part of the sensor which is exposed to the exhaust gases is surrounded by a protective device spaced from the sensor, which device consists of a porous tube of sintered material.

Surprisingly, when a tube of sintered material is used as protective device, the sensor is not inactivated, for practical purposes, over a long period of time by poisoning of the catalyst layer with compounds containing sulphur or phosphorus or with lead when conventional, lead-containing, fuels are used.

Porous ceramic materials such as sillimanite, cordierite, silica, corundum and forsterite are to be considered for the tube of sintered material, but metals or alloys such SIKA R (1.4404 or 316), Inconel (Registered Trade Mark), Incoloy, titanium, Monel (Registered Trade Mark), and nickel have proved specially suitable. Of these, the highly alloyed materials, such as Inconel and Incoloy, and nickel are to be preferred, because they are particularly resistant to exposure to temperatures of 900°C and above, as well as to gas oscillations and high thermal and mechanical stresses.

The wall thickness of the tube of sintered material should not be less than 1.5 mm in the case of

ceramic material and not less than 1 mm in the case of metal. If a wall thickness of 20 mm is exceeded, no substantially improved protective effect is achieved, but the time which the exhaust gases require to pass through the body of sintered material increases, as a result of which the response time of the probe increases. Wall thicknesses of 2 to 6 mm are preferred, as they combine a good protective effect with a short response time.

A range of pore size from 20 to 200 microns has proved suitable for the sintered material of the protective tube. Above a pore size of 800 microns, the protective effect is insufficient. Below 5 microns, the flow velocity decreases too sharply and the response time is excessively increased as a result. A low pore size permits of a small wall thickness, since the protective effect increases with diminishing pore size. Low flow velocity due to small pore size can be partly compensated for by small wall thickness. A pore size of 40 to 80 microns is preferred, because this ensures a particularly favourable compromise with respect to overall size, degree of deposition, stability, mechanical durability and gas-transit time through the sintered material.

The inner surfaces of the pores of the body of sintered material may be lined, for example by impregnation, with a catalyst material which accelerates the establishment of gas equilibrium, for example using precious metals, especially those of the platinum group. This has the advantage that it is possible, in simple fashion and practically without additional outlay apart from that for impregnation, to achieve a contact time which is long enough to bring the constituents of the exhaust gases into thermodynamic equilibrium, this being a prerequisite for the desired steep jump in potential of sensors of this type at an air-fuel ratio $\lambda = 1.000$, during the transition from the reducing state to the oxidising state and vice versa.

The manufacture of suitable tubes of sintered material is generally known and presents no difficulties to one skilled in the art. The protection body of sintered material may be joined to the body of the sensor by welding, soldering, screwing or clamping directly in front of the ceramic probe on the exhaust-gas side. It is possible to attach the protective body exchangeably, so that it can, if desired, be replaced, as an inexpensive component, before the protection has diminished, in which case the entire, expensive, sensor does not have to be renewed.

Two embodiments of the invention by way of example are illustrated in the accompanying drawing, in which:

Fig. 1 is a side view, partially cut away, of a sensor, in accordance with the invention, with a protective device of sintered material.

Fig. 2 is a section of the end part of another form of sensor in accordance with the invention, and Fig. 2 is a similar view of a sensor with a known form protective device.

The electromechanical measuring sensor illustrated in Fig. 1 operates, on the known principle of the oxygen-concentration chain, with ion-conducting solid electrolyte (so-called ceramic). It comprises an ion-conducting solid electrolyte tube 1, closed at one end, which is made of stabilised cubic zirconium dioxide. The tube 1 carries on its outside an electron-conducting catalyst layer 2 of platinum and is provided on its inside with an electron-conducting path 3 which extends into the region of the bottom of the said tube and may also be composed of platinum. The conducting path 3 is connected to connection means (not shown) which is in turn connected electrically to a plug-in contact 4. The tube 1 is fitted in gas-tight manner into the longitudinal bore 5 of a metallic housing 6, which is provided with a screw thread 7 for fitting into the wall of an exhaust pipe (not shown) and with a hexagon 8 for a spanner. Attached to the end of the housing 6 is a tube 9 provided with openings 10 for admitting ambient air into the cavity 11 in the tube 1. A portion of the tube 1 at the exhaust-pipe end projects beyond the bore 5 in the housing 6 and is exposed to the exhaust gases in the exhaust pipe. To protect the catalyst layer 2 on the tube 1 against intensive erosion and poisoning, as well as against the effects of temperature and pressure shocks due to direct impact of the stream of exhaust gases, a protective device 12 of sintered material is disposed around that region of the tube 1 which projects into the stream of exhaust gas and is attached by welding to the housing 6.

Fig. 2 illustrates another embodiment of the invention in which the protective device 12 of porous sintered material is detachably secured to the housing 6 by means of a screw thread 13.

Fig. 3 illustrates, for comparison, a known protective device consisting of a metal tube 14 having an opening 15 for admitting the exhaust gases.

The protective porous body 12 of sintered material ensures that the tube 1 is not exposed to the entire stream of exhaust gases. Only a part of the exhaust gases passes through the pores to the measuring sensor, so that, for practical purposes, a bypass effect is achieved. The quantity and velocity of the gas flow reaching the tube 1 can be simply controlled by varing the wall thickness and pore size of the body 12 of sintered material and made to conform with desired conditions. Furthermore, by virtue of the body of sintered material, it is possible to modulate oe qualise the temprature of the probe tub 1. The solid lectrolyt tub ("ceramic") is protected against temprature shocks and pressure paks. At low gas temperature, that is t say when an ngine is idling, the sensor cools less quickly, with the result that a probe 1 provided with a protective d vice in accordance with the invention does not become inoperative as quickly as a known probe. Since only a relatively small flow of gas reaches the sensor because of the bypass effect of the porous body 12 f sintered material, it is also relatively simpl to heat the sensor, which is advantageous for cold starting and, possibly, also for idling. As th

body 12 has a damping effect on temperature and pressure peaks, the sensor can be fitted closer to the engine, thus reducing the response time of the sensor. The small delay which the gas flow experiences, before it encounters the sensor, due to its passage through the porous body 12, can therefore be readily compensated for.

The effectiveness of a protective device in accordance with the invention is illustrated by the following example.

EXAMPLE

A commercial sensor of stabilised zirconium dioxide lined on both sides with precious metal was surrounded by a protective device 12 as illustrated in Fig. 1. The device was made of sintered SIKA R, material number: 1.4404, and had a wall thickness of 3.0 mm and pore size of 80 microns.

The measuring sensor provided with the protective device was exposed to the exhaust gases of an Otto-type engine for 45 hours. The engine consumed 8 litres of petrol per hour, the petrol being treated with 0.15 g of lead per litre. Within this time, practically no significant impairment of the response times for the voltage jump from rich to lean and from lean to rich mixture occurred. Also, the air-fuel ratio (λ) corresponding to a specific voltage remained largely constant. The sensor also retained its good sensitivity due to the fact that the temperature required to generate a specific voltage (at $\lambda = 0.98$) remained practically constant. All the values determined lie within the specified values laid down by the manufacturer for a new probe (without the protective device in accordance with the invention). The results obtained are set out in the following table:

TABLE

Test Period [h]		According to the invention as Fig. 1		Values specified by the manufacturer of the sensor
		0	45h	
Response time for the voltage jump from rich to lean (600–400mV)	at 350°C [msec]	200	240	<400
	at 550°C [msec]	10	20	<30
Response time for the voltage jump from lean to rich (400–600mV)	at 350°C [msec]	18	30	<65
	at 550°C [msec]	12	40	<40
λ at 500mV		1.012	1.014	1.003 to 1.018
Temperature for U_S = 500mV		230	235	<265

For comparison, a sensor without a protective device in accordance with the invention was exposed to the stream of exhaust gases. Even after just 3 hours, the maximum voltage of 900 mV delivered initially by the sensor collapsed to about 400 mV, that is the sensor was rendered useless after 3 hours.

CLAIMS

1. An electromechanical measuring sensor for determining the oxygen content in exhaust gases, in which the part of the sensor which is exposed to the exhaust gases is surrounded by a protective device spaced from the sensor, which device consists of a porous tube of sintered material.

2. A sensor according to Claim 1, wherein the sintered material is metallic.

3. A sensor according to Claim 2, wherein the tube of sintered material is made of a highly temperature-resistant nickel alloy of alloys.

4. A sensor according to any one of Claims 1 to 3, wherein the tube of sintered material is spaced from the sensor by 0.01 to 20.0 mm.

5. A sensor according to any one of Claims 1 to 4, wherein the tube, if made of sintered ceramic material, has a wall thickness of 1.5 to 20 mm and, if made of sintered metallic material, a wall thickness of 1 to 20 mm.

6. A sensor according to any one of Claims 1 to 5, wherein the sintered material of the tube has a pore size of 5 to 800 microns.

7. A sensor according to any one of Claims 1 to 6, wherein the inner surfaces of the pores of the sintered material of the tube are lined with a catalyst material which accelerates the establishment of gas equilibrium.

8. An electrochemical measuring sensor for determining the oxygen content in exhaust gases substantially as hereinbefore described with reference to Figs. 1 and 2 of the accompanying drawing.

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